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# Direct cleavage of sorbitol from oligosaccharides via a sequential hydrogenation-hydrolysis pathway

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ABSTRACT

The production of sorbitol from polysaccharides is widely believed to proceed via hydrolysis to glucose and subsequent hydrogenation. Nevertheless, our previous study on the hydrolytic hydrogenation of cellobiose confirmed simultaneous hydrolysis and hydrogenation with a higher kinetic selectivity of hydrogenation over hydrolysis. Herein, kinetics of hydrogenolysis of trisaccharides with α-1,4 and β-1,4 glycosidic linkages were studied using Ru/C in combination with a molecular acid as catalyst system. Kinetic analysis emphasises a fast hydrogenation of the reducing end of trisaccharides followed by a facilitated cleavage of the terminal sorbitol unit. Considering the obtained reaction rate constants, hydrogenation compared to hydrolysis proceeds up to 24 and 15 times faster for maltotriose and cellotriose, respectively. Additionally, superior reaction rate constants and decreased activation energies for hydrolytic cleavage of sorbitol can be observed. Hence, a sequential hydrogenation-hydrolysis pathway clearly contributes to sorbitol formation based on oligosaccharides.



## 1. Introduction

Increasing concerns about future energy supply and the environmental impact of fossil fuels have enforced the society to find renewable resource alternatives. Biomass, both renewable and environmentally friendly, is considered to be one of the best alternatives [1,2]. Lignocellulose and starch-based materials are the most abundant source of biomass. Recently, the production of biofuels and value-added chemicals from cellulose and starch has gained much attraction [3–5]. Special attention has been devoted to the conversion of polysaccharides into sorbitol which has been proposed as potential platform chemical for the production of fuels, monomers for polymer industries and as feedstock for renewable hydrogen production [4,6,7]. Additionally, sorbitol and its secondary products are already used today, e.g. as sweetening agent, for the production of surfactants and in pharmaceutical industry [8].

Sorbitol can be produced selectively, e.g. via hydrogenation of a hydrolysed starch solution in the presence of catalysts such as Raney nickel or Ru/C [9]. Also a direct transformation of cellulose into sorbitol has been demonstrated, e.g. cellulose can be converted into sorbitol in the presence of molecular acids such as $H_2SO_4$, HCl or heteropoly acids together with supported metal catalysts (Pt, Pd and Ru) [10–15]. Combined with a mechanocatalytic prehydrolysis of cellulose to cellooligomers, Schüth and co-workers [16] achieved up to 94% yield of sorbitol based on cellulose.

Despite numerous studies on production methods, a fundamental understanding of the reaction and kinetics of a conversion of polysaccharides to sorbitol is hardly available, mostly because of the complex molecular structure of polysaccharides. It is generally believed that the conversion of polysaccharide to sorbitol passes through hydrolysis to monosaccharides consecutively followed by hydrogenation to sorbitol [17–19].

In contrast, our pervious investigation and studies by the groups of Wang et al. and Makkee et al. on the hydrolytic hydrogenation of cellobiose as model molecule of cellulose confirmed a direct hydrogenation to cellobitol (3-β-D-glucopyranosyl-D-glucitol) followed by hydrolysis as alternative reaction pathway [20,21]. Our kinetic analysis revealed that this reaction pathway can contribute significantly to sorbitol formation [22]. Consequently, the question arises whether a selective formation of sorbitol via hydrogenation followed by hydrolysis should also be considered for oligo- and polysaccharides, respectively. Therefore, the study is extended to include trisaccharides which sufficiently resemble polysaccharides and still have a relatively simple structure. The trisaccharides, cellotriose (β-linked D-glucose) based on cellulose and maltotriose (α-linked D-glucose) based on starch were chosen for this study (Fig. 1).

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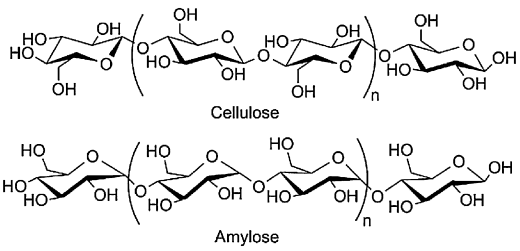



**Fig. 1.** Structure of cellulose and amylose.

The aim is to understand the role of hydrogenation-hydrolysis sequences within the overall reaction network. In the present study, a heteropoly acid (silicotungstic acid, $H_4[W_{12}SiO_{40}]$) combined with a supported ruthenium catalyst (5 wt% Ru/C) have been used as catalytic system due to high selectivity for sorbitol production [10,13,14,22]. A systematic kinetic analysis has been carried out providing a quantitative interpretation of the reaction pathways paving the way for a novel view on the transformation of oligosaccharides and potentially polysaccharides into sorbitol.

## 2. Materials and methods

Maltotriose, maltotriitol, maltose, maltitol, glucose, sorbitol, the heteropoly acid (HPA, silicotungstic acid) and 5 wt% Ru/C were purchased from Aldrich. Cellotriose and cellotriitol were supplied by Megazyme, and cellobiose was purchased from Alfa Aesar. All the above-mentioned chemicals were of analytical grade and used without further purification. Cellobitol was self-synthesized with a purity of 99% and characterized by $^{13}C$ NMR spectroscopy. All experiments were performed three times in a batch-type high-pressure autoclave reactor. Typically, trisaccharides (2 mmol), Ru/C (0.1 g) and heteropoly acid (0.2 g) were added into a Teflon-lined stainless steel reactor precharged with $H_2O$ (20 $cm^3$). The reactor was flushed several times with $N_2$ and $H_2$ at room temperature. The reactor was pressurized with $H_2$ and then preheated to the defined temperature. The reaction was operated at a pressure of 4 MPa, a temperature range of 393–433 K and a stirring speed of 800 rpm. Time zero was set at the beginning of the isothermal reaction stage. The reactor was equipped with a sampling valve and the progress of the reaction was monitored by periodically taking sample from the autoclave. Samples were filtered through a 25 μm nylon filter prior to analysis. Analyses of products were performed using an HPLC system consisting of a ligand exchange column (Shodex sugar SZ5532, 6 mm × 150 mm) and an RI detector. The eluent was an aqueous solution of acetonitrile and water at a flow rate of 1 mL $min^{-1}$. The column was operated at 323 K and sample analysis was completed within 50 min. The samples were dissolved in acetonitrile (1:1) prior to injection into the HPLC system. The concentration of each compound in the product mixture was determined using calibration curves of pure compounds in standard solutions.

## 3. Results and discussion

### 3.1. Reaction network analysis

Our analysis suggests that in the presence of a supported metal catalyst (Ru/C) and a molecular acid (HPA, silicotungstic acid), the catalytic conversion of trisaccharides proceeds via a network of parallel and consecutive reactions (Scheme 1). The hydrolysis of trisaccharides (cellotriose or maltotriose) to the corresponding disaccharides (cellobiose or maltose) and glucose as well as the hydrogenation to the reduced trisaccharides (cellotriitol or maltotriitol) can be observed.

The hydrolysis of reduced trisaccharides yields either a disaccharide and sorbitol or a reduced disaccharide (cellobitol or maltitol) and glucose. In subsequent transformations, the disaccharide can be either hydrolysed to glucose or hydrogenated to the reduced form which can be further hydrolysed to glucose and sorbitol. It should be noted that trisaccharides have two different glycosidic bonds that can be hydrolysed [23,24]. Here, the cleavage of these two glycosidic bonds is not distinguished.

Fig. 2 shows the time evolution of product formation at different reaction temperatures for the conversion of cellotriose to sorbitol. The product distribution at different reaction temperatures illustrates a significant contribution of a prior hydrogenation of the substrate to the reduced form. This effect is favoured at lower reaction temperatures.

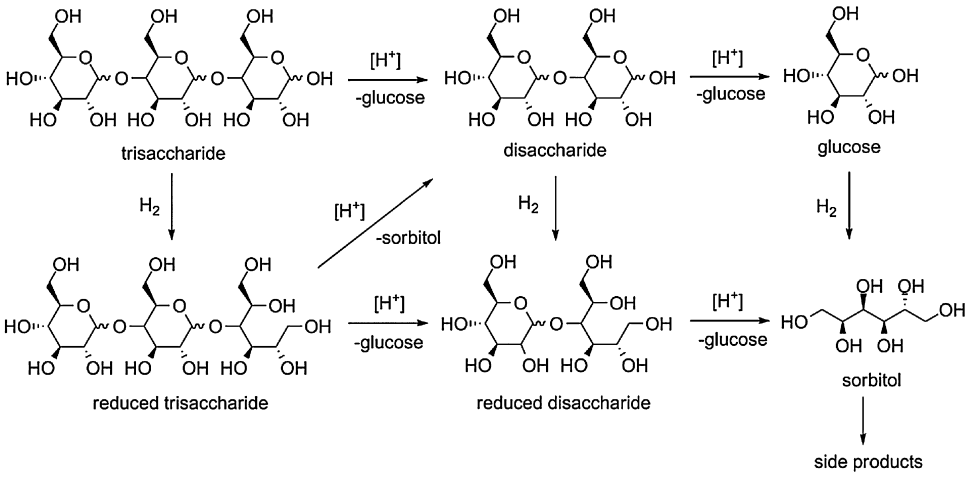
Cellotriitol, the hydrogenation product of cellotriose, is the major product with a maximum yield of 69% at 393 K (Fig. 2a). As the reaction temperature increases, the yield of cellotriitol decreases. At the same time, the yield of the target product sorbitol increases reaching a maximum of 74% at 443 K (Fig. 2c). Cellobiose presents a potential reaction intermediate and is simultaneously converted via two catalytic pathways: (1) hydrogenation to cellobitol and (2) hydrolysis to glucose. At lower reaction temperatures, a higher cellobitol yield can be observed which again points out the preferential hydrogenation of cellobiose over its hydrolysis. For all reactions, only small amounts of glucose were observed. We relate this to the direct formation of sorbitol through hydrolysis of cellotriitol together with a fast hydrogenation of glucose to sorbitol [25].

Under the applied reaction condition, no side reactions based on glucose, e.g. via dehydration to 5-hydroxymethylfurfural or levulinic acid, were observed and degradation products from sorbitol including sorbitan and isosorbide were negligible. In the described temperature range, carbon balances could be closed with mean carbon balances of above 95% based on threefold experiments and no humin formation was observed. Overall, these findings suggest that the hydrogenation of substrates and intermediates proceeds faster compared to hydrolysis. Unlike a simple hydrolysis to glucose, trisaccharides are mainly converted via hydrogenation-hydrolysis sequences.

### 3.2. Kinetic assessment of reaction sequences

A kinetic analysis of the reaction network has been carried out to quantify the relative contribution of the different reaction pathways. Both hydrolysis and hydrogenation reactions are assumed to follow pseudo-first-order kinetics [22,26]. The concentrations of each compound as a function of time as well as the curve fittings are summarized in the supplementary information (ESI). Additionally, reference experiments of the individual reactions have been carried out confirming the major role of the individual catalyst compounds in the overall reaction network (ESI, Fig. S2). Indeed, over Ru/C maltotriitol is the major product, while in the presence of silicotungstic acid maltose and glucose form. Kinetic rate constants are solved using the least-square optimization algorithm relative to the experimental data. Temperature dependency of the rate constants are taken into account using Arrhenius equation within the range of 373–433 K.

Cellotriose and maltotriose exhibit a comparable behaviour. In the following, cellotriose is discussed comprehensively. From Scheme 2 and for cellotriose, the hydrolysis reactions include hydrolysis of cellotriose ($k_1$), cellotriitol ($k_3$, $k_4$), cellobiose ($k_6$) and cellobitol ($k_7$). The hydrogenation reactions comprehend the hydrogenation of cellotriose ($k_2$), cellobiose ($k_5$) and glucose ($k_8$). As mentioned previously, for hydrolysis of cellotriose, the cleavage of bonds is not distinguished. Therefore, the rate constant is




**Scheme 1.** Representation of the reaction network of the catalytic conversion of trisaccharides to sorbitol.

the sum of the rate constants for the hydrolysis of both bonds. The apparent rate constants and activation energies for hydrolysis and hydrogenation steps of trisaccharides are summarized in Table 1. Below 433 K, the rate constant $k_2$ (cellotriose to cellotriitol) is significantly higher than the rate constant $k_1$ (cellotriose to cellobiose and glucose) confirming a fast hydrogenation to cellotriitol. The rate constant $k_3$ for hydrolysis of cellotriitol to cellobiose and sorbitol is slightly higher compared to $k_4$ (cellotriitol to cellobitol and glucose) indicating that the hydrolysis of the glycosidic bond close to the reducing end is easier as cleavage of the glycosidic bond adjacent to the non-reducing end of cellotriitol.

In the case of cellobiose similar to cellotriose, the hydrogenation reaction is notably faster compared to hydrolysis at lower temperatures. Additionally, the rate constant for hydrolysis of cellobitol $k_7$ is higher than the rate constant for hydrolysis of cellobiose $k_6$ confirming again a facilitated hydrolysis after hydrogenation. A closer look on the observed activation energies strengthens this interpretation. The activation energies $E_3$ and $E_4$ for hydrolysis of cellotriitol were determined to be 133 and 139 kJ mol$^{-1}$, respectively, compared to $E_1$ with 147 kJ mol$^{-1}$ for the hydrolysis of cellotriose emphasising again a facilitated hydrolysis after hydrogenation. This trend reoccurs for the hydrolysis of cellobiose with an activation energy $E_6$ of 128 kJ mol$^{-1}$ compared to $E_7$ with 119 kJ mol$^{-1}$ for

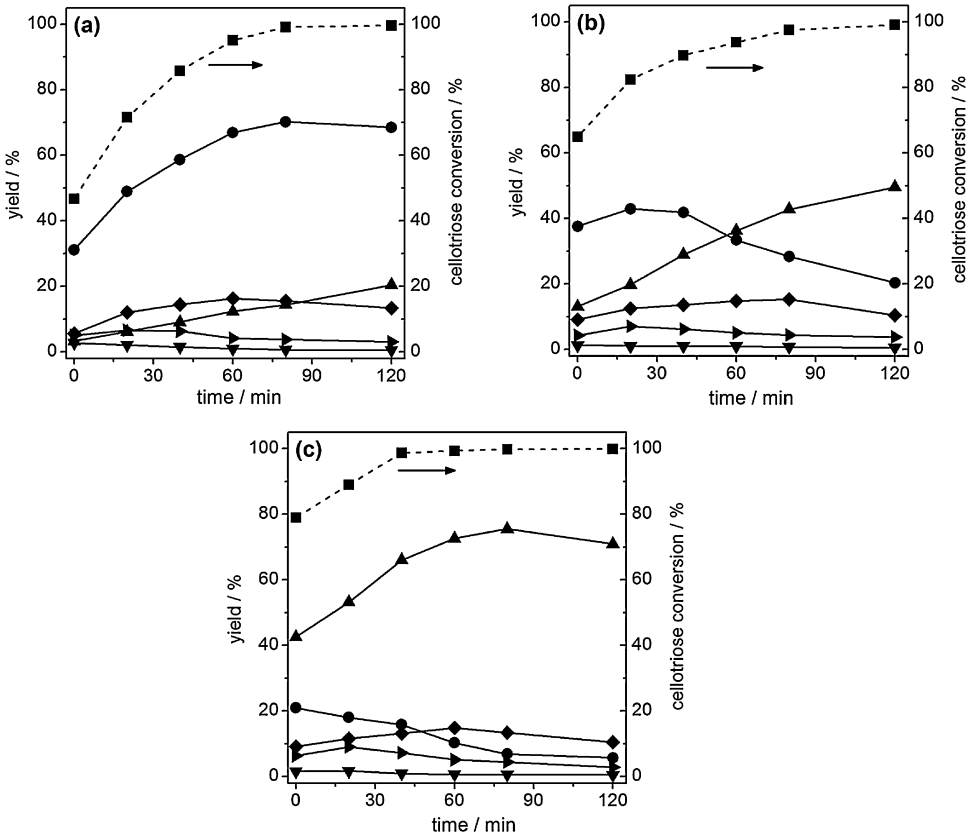
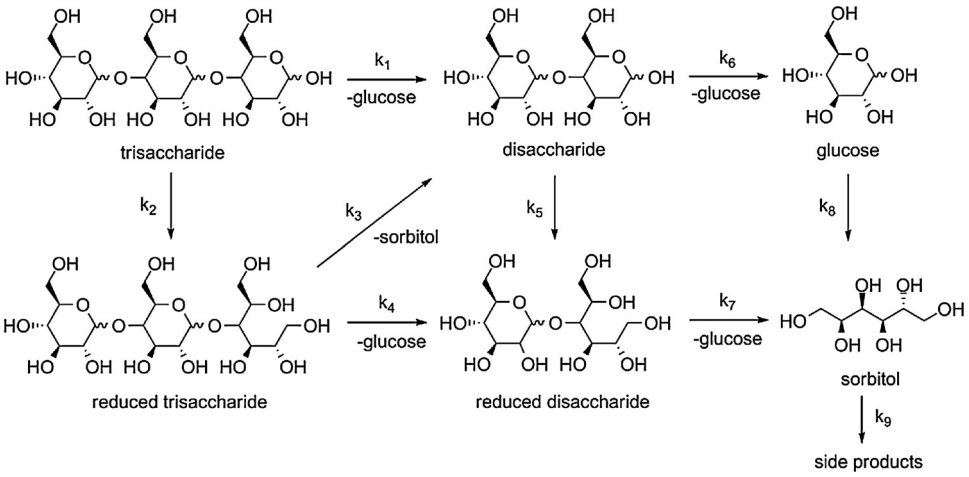



**Fig. 2.** Yield of cellotriitol (●), cellobiose (►), cellobitol (♦), sorbitol (▲), glucose (▼) and cellotriose conversion (■) as a function of elapsed time (a) 393, (b) 413 and (c) 433 K. Reaction conditions: cellotriose, 2 mmol; Ru/C, 0.1 g; HPA, 0.15 g; $H_2O$, 20 cm$^3$, 4 MPa $H_2$.




**Scheme 2.** Representation of the reaction network of the catalytic conversion of trisaccharides to sorbitol.

**Table 1**
Kinetic parameters for catalytic conversion of trisaccharides to sorbitol.

| $T$ (K) | Cellotriose | | | | Maltotriose | | | |
|---|---|---|---|---|---|---|---|---|
| | 393 | 413 | 433 | $E_a$ (kJ mol$^{-1}$) | 393 | 413 | 433 | $E_a$ (kJ mol$^{-1}$) |
| $k_1$ ($10^{-1}$ min$^{-1}$) | 0.0015 | 0.017 | 0.101 | 147 | 0.0025 | 0.035 | 0.101 | 131 |
| $k_2$ ($10^{-1}$ min$^{-1}$) | 0.022 | 0.146 | 0.315 | 94 | 0.0612 | 0.26 | 0.653 | 84 |
| $k_3$ ($10^{-1}$ min$^{-1}$) | 0.0036 | 0.040 | 0.156 | 133 | 0.0075 | 0.102 | 0.201 | 117 |
| $k_4$ ($10^{-1}$ min$^{-1}$) | 0.0023 | 0.027 | 0.116 | 139 | 0.0041 | 0.071 | 0.141 | 126 |
| $k_5$ ($10^{-1}$ min$^{-1}$) | 0.0617 | 0.283 | 0.601 | 80 | 0.108 | 0.418 | 0.985 | 77 |
| $k_6$ ($10^{-1}$ min$^{-1}$) | 0.0062 | 0.061 | 0.235 | 128 | 0.011 | 0.103 | 0.281 | 112 |
| $k_7$ ($10^{-1}$ min$^{-1}$) | 0.0092 | 0.087 | 0.265 | 119 | 0.021 | 0.184 | 0.352 | 101 |
| $k_8$ ($10^{-1}$ min$^{-1}$) | 0.109 | 0.357 | 0.810 | 71 | 0.26 | 0.81 | 1.51 | 62 |

cellobitol hydrolysis. Activation energies $E_2$, $E_5$ and $E_8$ for the hydrogenation reactions were estimated to be 94, 80 and 71 kJ mol$^{-1}$ are in good agreement with our previous report and literature values [22].

One also has to take notice that the activation energies of hydrogenation increase as the chain length of saccharides increases. This indicates a facilitated hydrogenation of shorter saccharides over the longer ones. The same holds for hydrolysis reactions for which the longer chains have greater activation energies $E_6 < E_1$. This observation is in agreement with reports on the rate of hydrolysis of cellodextrins which increases with the degree of polymerization (DP) [27,28]. It should be noted that the hydrolysis of oligosaccharides is certainly affected by geometric constrains such as the anomeric configuration of the glycosidic linkages (α or β), the position of linkage such as (1–4), (1–6), the presence of functional groups in the molecule and the intensity of inter- and intramolecular interactions. For instance, the α-1,4-glycosidic bond is expected to hydrolyse more readily than the β-1,4 glycosidic linkage [29,30].

Based on these observations, the question arises whether a preferential hydrogenation of oligosaccharides followed by hydrolysis to release sorbitol presents a significant reaction pathway in hydrogenolysis of such feedstocks. The present study confirms a tremendous effect of oligosaccharide hydrogenation. To ratio-

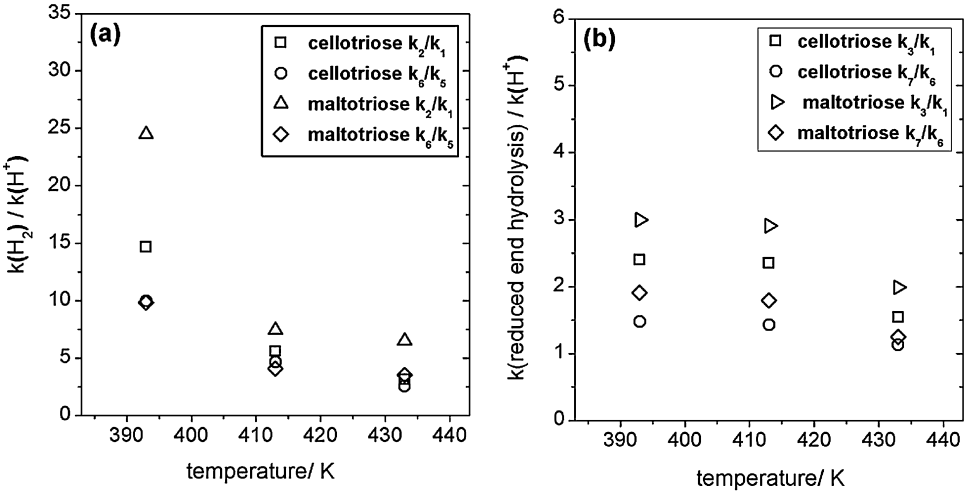



**Fig. 3.** Kinetic selectivity of hydrogenation versus hydrolysis (a) and hydrolysis of reduced end versus non-reduced end (b) at different reaction temperatures (Table 1).

nalise the obtained results, the ratios of reaction rate constants for hydrogenation versus hydrolysis of cellotriose and maltotriose were summarized (Fig. 3). Despite a facilitated hydrolysis of α-1,4-glycosidic bonds in maltose and maltotriose, hydrogenation remains to be superior to hydrolyse especially at lower temperatures. The dominant character of hydrogenation is even more pronounced for longer oligomers. Comparing the ratio of $k_2/k_1$ versus $k_5/k_6$, a maximum decrease from 24 to 10 and 15 to 10 for maltotriose and cellotriose, respectively, becomes obvious (Fig. 3a). For all temperatures, the kinetic selectivity of hydrogenation versus hydrolysis is more pronounced for the investigated trisaccharides compared to the corresponding disaccharides under the applied reaction conditions.

The kinetic selectivity for hydrolysis of reduced compounds with regard to hydrolysis of the corresponding saccharide adds to the described effects (Fig. 3b). Indispensable of α-1,4 or β-1,4 glycosidic linkages, a facilitated hydrolysis after hydrogenation occurs. Important to note that the trend is even more distinct for hydrolysis of longer oligosaccharides ($k_7/k_6$ vs. $k_3/k_1$ for cellotriose and maltotriose). From a structural point of view, these data emphasise an accelerated hydrolysis of oligosaccharides in open ring structures compared to hydrolysis of the close structure.

Therefore, our analyses confirm that the chain length has an influence on the kinetic selectivity for hydrolysis and hydrogenation and hydrolysis after hydrogenation. A progressive decrease in the rate constants with increasing size of the oligosaccharide can be observed. Together with overall higher rate constants for hydrolysis of reduced compounds, a sequential hydrogenation followed by hydrolysis to release sorbitol could even present an important reaction pathway in the case of longer oligosaccharides. However, it should be noted that the presented kinetic analysis can only support the proposed reaction network but not confirm the reaction sequence. Future investigations will aim for a theoretical and experimental validation of this hypothesis utilizing mixed oligomeric substrates for sorbitol production.

## 4. Conclusions

Trimeric oligosaccharides have been studied as substrates for the formation of sorbitol. Hydrogenation of such oligosaccharides followed by a facilitated hydrolysis of the terminal sorbitol unit could also be observed. A time-resolved study and kinetic analysis emphasise this reaction pathway to be preferred at low reaction temperatures and for longer oligomers. The kinetic selectivity of hydrogenation versus hydrolysis increases with oligomer size reaching a ratio of 24 and 15 at 393 K for maltotriose and cellotriose, respectively. A generalised conclusion on sorbitol formation based on other oligosaccharides, e.g. mixtures of cellooligomers, available via pre-treatment of cellulose could be premature. Nevertheless, our observations clearly show the significance of the described pathway of sorbitol production. Especially at lower temperatures and with increasing oligomer size, a preferential hydrogenation and hydrolysis of the terminal sorbitol unit needs to be considered. In this regard, hydrogenolysis of oligosaccharides such as starch and cellulose should be revisited from a mechanistically point of view. Future studies will aim for insights concerning the impact of sorbitol formation via direct cleavage of technically relevant oligomer mixtures, e.g. dextrins and cellooligomers.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2014.11.049.

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